

# PATENT ABSTRACTS OF JAPAN

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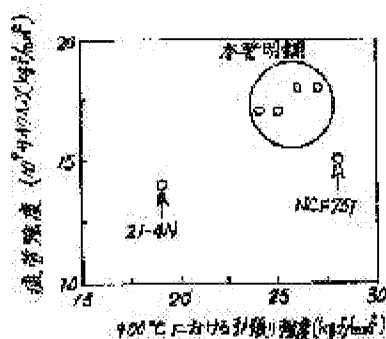
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## (54) HEAT RESISTANT STEEL FOR EXHAUST VALVE

(57)Abstract:

**PURPOSE:** To obtain a heat resistant steel for exhaust valve capable of securing economical efficiency and hot workability and excellent in strength at high temp. and fatigue strength at high temp. by specifying a composition consisting of C, Si, Mn, Cr, Ni, V, N, and Fe.

**CONSTITUTION:** The heat resistant steel for exhaust valve which has a composition consisting of, by weight, 0.3-0.6% C, 0.1-1.0% Si, 8.0-11.0% Mn, 19.0-25.0% Cr, 3.0-10.0% Ni, 0.3-1.0% V, 0.3-0.6% N, and the balance Fe with inevitable impurities and containing, if necessary, prescribed amounts of Mo and W and where high temp. tensile strength at 900°C is regulated to >23kgf/mm<sup>2</sup> and also rotating bending fatigue strength at 900°C is regulated to >16kgf/mm<sup>2</sup> is obtained.



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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This inventions are high temperature members, such as an exhaust valve of internal-combustion engines, such as a car, and relate to heat resisting steel excellent in high temperature strength or fatigue-at-elevated-temperature intensity.

[0002]

[Description of the Prior Art]In recent years, the fuel consumption improvement and a high increase in power of a car are desired, and exhaust gas temperature has also been rising even near 900 \*\* in connection with this. although 21-4N steel (SUH35:0.5C-9Mn-21Cr-4nickel-0.4N) has so far been widely used as charges of exhaust valve material, such as an automobile gasoline engine, -- this steel -- the temperature rise of exhaust gas - - correspondence -- it has neither sufficient high temperature strength nor fatigue-at-elevated-temperature intensity. Although it may be coped with by using the Ni group alloy of NCF751 grade from a viewpoint that the high temperature strength of 21-4N is insufficient, The fatigue-at-elevated-temperature intensity of not less than 850 \*\* is the level mostly with 21-4N also NCF751, and since a Ni group alloy is also a high cost, its balance of cost performance is insufficient. Partly, in order to lower the temperature of an exhaust valve, it hollow-izes and is coped with by carrying out Na enclosure. However, hollow-ized processing becomes a high cost and Na has the problem that handling is dramatically difficult and is accompanied by danger.

[0003]

[Problem(s) to be Solved by the Invention]As mentioned above, in the conventional charge of exhaust valve material. It has the problem referred to as being a high cost or being accompanied by product handling top danger for the case where it is insufficient in respect of the elevated-temperature characteristic, especially fatigue-at-elevated-temperature intensity, highly-efficient-izing (use of a Ni group alloy) of a raw material, or valve materials' low-temperature-izing (hollow valve) to the temperature rise of exhaust gas. An object of this invention is to provide the heat resisting steel for exhaust valves which has improved high temperature strength and fatigue-at-elevated-temperature intensity without degrading hot-working nature, securing economical efficiency. That is, while making the minimum a change of the construction material of mating members, such as a valve seat, in order to secure economical efficiency, 21-4N steel is made into a fundamental component, and an improvement of high temperature strength and fatigue-at-elevated-temperature intensity is aimed at by adding a proper quantity of V, Mo, or W to this.

[0004]

[Means for Solving the Problem]In order that this invention may make the present 21 to 4 steel basic composition from a viewpoint of securing economical efficiency and may raise high temperature strength and fatigue-at-elevated-temperature intensity of this, it is what makes it basic technique thought to use precipitation strengthening and solid solution strengthening, The 1st invention is constituted in order to aim at an improvement of high temperature strength by precipitation strengthening, and fatigue-at-elevated-

temperature intensity. That is, precipitation strengthening was taken as precipitation strengthening by carbon nitride by V independent addition in consideration of that the amount of strengthening is large, and especially a thing that the amount of strengthening and temperature dependence of strengthening change with kinds of \*\* sludge compared with \*\* solid solution strengthening. If 21-4N and NCF751 which are conventional materials are compared as shown in drawing 1 - 3, NCF751 has high intensity compared with 21-4N over a total temperature region, but the difference will become so small that it becomes an elevated temperature, and high temperature strength of both \*\* will be mostly set to the level at 950 \*\*. Although NCF751 has high fatigue strength about fatigue-at-elevated-temperature intensity compared with 21-4N by the low temperature side too, if it becomes 900 \*\*, fatigue strength of both \*\* will be mostly set to the level. This comes from a difference in an elevated-temperature strengthening mechanism of both \*\*, and is because NCF751 is precipitation strengthening according to gamma' to 21-4N being precipitation strengthening by carbon nitride, Precipitation strengthening of gamma' has strong temperature dependence compared with precipitation strengthening of carbon nitride, and if it becomes an elevated temperature, as for precipitation strengthening of gamma', an effect will fade remarkably. Paying attention to this point, elevated-temperature strengthening by precipitation-strengthening + solid solution strengthening of carbon nitride was attained. It found out that independent addition of V was the most effective also in a carbon nitride formation element. Although it was effective for elevated-temperature strengthening also about a carbon nitride formation element called Ti, Nb, Ta, or Zr, it is not as an effect of V and V and these compound addition found out that it was what checks an effect of V. If compound addition of the element with large affinity with C and N is carried out rather than V like [ this has the carbon nitride of V most effective in elevated-temperature strengthening, and ] Ti or Nb, an effect of \*\* and V that carbon nitride of V becomes difficult to deposit will fade. Therefore, as precipitation strengthening, an improvement of high temperature strength and fatigue-at-elevated-temperature intensity is aimed at in carbon nitride precipitation strengthening by independent addition of V.

[0005]the 2nd invention is Mo, or independent or a thing which tries to attain solid solution strengthening by compound addition of W as a method for strengthening further, without checking such an effect of V. It found out that Mo which can secure the amount of dissolution as a solid-solution-strengthening element in a not less than 700 \*\* temperature region, or W was independent, or compound addition was effective. Since the solid solution strengthening can secure high temperature strength etc. which were stabilized for a long time compared with precipitation strengthening, the 3rd invention is the effective strengthening technique to fatigue at elevated temperature or longtime creep, When not adding V, it is Mo with solid-solution-strengthening ability high as a method, or independent or a thing based on having found out that especially compound addition was effective in improvement in fatigue-at-elevated-temperature intensity of W which raises high temperature strength and fatigue-at-elevated-temperature intensity.

[0006]

[Function]The reason for limitation of the addition of the alloy element in this invention is explained below.

C: It was an alloying element indispensable to precipitation strengthening, and in order to secure high temperature strength and fatigue-at-elevated-temperature intensity, it could

be 0.3% or more. On the other hand, the addition exceeding 0.6% made this the maximum in order to reduce hot-working nature, cutting ability, and ordinary temperature ductility.

[0007]Si: It used as deoxidation material, and since it was effective in oxidation-resistant improvement, it could be 0.1% or more. On the other hand, the addition exceeding 1.0% made this the maximum in order to reduce ordinary temperature ductility.

Mn: It is an austenite formation element and not less than 8.0% needs to be added. On the other hand, the addition exceeding 11.0% made this the maximum in order to check oxidation resistance.

Cr: It could be not less than 19.0% for oxidation-resistant reservation. The further oxidation-resistant improvement does not have the addition exceeding 25.0%, and it made this the maximum in an about 800-900 \*\* temperature region.

[0008]nickel: It was an austenite formation element, and since it was effective in the improvement in heat-resistant, it could be not less than 3.0%. However, since austenite stability and the contribution of the improvement in heat-resistant became small, the addition exceeding 10.0% made this the maximum.

V: It is an element indispensable to an improvement of the high temperature strength by precipitation strengthening, and fatigue-at-elevated-temperature intensity. Carbon nitride of V is an effective sludge in order to raise high temperature strength and fatigue-at-elevated-temperature intensity comparatively compared with other carbon nitride, since it is [ / high temperature long time ] stable. On the other hand, in independent addition (claim 1), superfluous addition could be 0.3 to 1.0% from a viewpoint of high temperature strength and fatigue-at-elevated-temperature intensity, hot-working nature, and ordinary temperature ductility in order to cause the fall of hot-working nature and ordinary temperature ductility. In compound addition with Mo and/or W which are solid-solution-strengthening elements (claim 2), in order that addition of Mo and/or W might also degrade hot-working nature, it needed to be made the addition lower than the case of V independent addition, and could be 0.1 to 0.7%.

[0009]N: It was an alloying element indispensable to precipitation strengthening, and in order to secure high temperature strength and fatigue-at-elevated-temperature intensity, it could be 0.3% or more. On the other hand, the addition exceeding 0.6% made this the maximum in order to reduce hot-working nature, cutting ability, and ordinary temperature ductility.

Mo: It is an element indispensable to an improvement of the high temperature strength by solid solution strengthening, and fatigue-at-elevated-temperature intensity. Compared with precipitation strengthening, the amount of strengthening excels [ solid solution strengthening ] in the prolonged stability of the small thing. On the other hand, superfluous addition reduces hot-working nature remarkably. For this reason, by claim 2 which is a case of 1.0 to 5.0%, and compound addition with V in claim 3 which is a V additive-free case, it could be 0.5 to 5.0% from a viewpoint of coexistence with high temperature strength and fatigue-at-elevated-temperature intensity, hot-working nature, and ordinary temperature ductility. By W and composite, in the V additive-free case, it was considered as  $1.0\% \leq \text{Mo} + \text{W} \leq 7.0\%$ , and, in V addition, could be  $0.5\% \leq \text{Mo} + \text{W} \leq 5.0\%$ .

[0010]W: It is an element indispensable to an improvement of the high temperature strength by solid solution strengthening, and fatigue-at-elevated-temperature intensity.

Compared with precipitation strengthening, the amount of strengthening excels [ solid solution strengthening ] in the prolonged stability of the small thing. On the other hand, superfluous addition reduces hot-working nature remarkably. For this reason, by claim 2 which is a case of 1.0 to 5.0%, and compound addition with V in claim 3 which is a V additive-free case, it could be 0.5 to 5.0% from a viewpoint of coexistence with high temperature strength and fatigue-at-elevated-temperature intensity, hot-working nature, and ordinary temperature ductility. By Mo and composite, in the V additive-free case, it was considered as  $1.0\% \leq \text{Mo} + \text{W} \leq 7.0\%$ , and, in V addition, could be  $0.5\% \leq \text{Mo} + \text{W} \leq 5.0\%$ .

[0011]High temperature strength and fatigue-at-elevated-temperature intensity : In order to fulfill that it is higher than  $23 \text{ kgf(s)/mm}^2$  at the tensile strength of 900 \*\*, and the rotary bending fatigue strength of 900 \*\* is higher than  $15 \text{ kgf(s)/mm}^2$ , V, Mo, or W is made to attain by independent or carrying out compound addition like the above-mentioned chemical entity.

[0012]

[Example]The chemical entity of this invention steel and comparison steel is shown in Table 1, and the hot-working nature and the construction material characteristic of sample offering steel are shown in Table 2, respectively. After carrying out hot forging of the sample offering steel and carrying out a solution treatment at 1175 \*\* after a vacuum ingot, it gave prescription of air cooling after the 760 \*\*x 4-hour retention, and extracted various specimens.

[0013]As shown in Table 2, J steel added exceeding 1.0% by independent addition (claim 1) of V is a grade where is not good and a surface check occurs at the time of a forge and which can perform specimen extraction once. [ of hot-working nature ] Superfluous addition of V degrades hot-working nature and ordinary temperature ductility in the value in which ordinary temperature ductility is also below 10%. As compared with B steel which added 0.87% of V, there is no big difference about high temperature strength and fatigue-at-elevated-temperature intensity, and even if it adds V exceeding 1%, the further improvement in high temperature strength and fatigue-at-elevated-temperature intensity cannot be found. It turns out that high temperature strength and fatigue-at-elevated-temperature intensity are securable from comparison of A steel and 21-4N steel by adding V 0.3% or more.

[0014]Mo, and W and V -- compound addition -- carrying out (claim 2) -- comparison with C-E steel and 21-4N steel shows that high temperature strength and fatigue-at-elevated-temperature intensity are improved, and the ductility of ordinary temperature can also be secured. If Mo exceeds 5% on the other hand so that the example of K steel may show, and if it exceeds 5% by Mo+W, hot-working nature will deteriorate, and cracks will occur frequently at the time of a forge. If it exceeds 0.7% when carrying out compound addition with Mo and W, hot-working nature will deteriorate, as the example of M steel furthermore shows also about V.

[0015]If Mo and W are added (claim 3), compared with 21-4N, high temperature strength and fatigue-at-elevated-temperature intensity are improved so that the example of F - H steel may show, and the ductility of ordinary temperature can also be secured. However, if W exceeds 5% so that the example of L steel may show, and if it exceeds 7% by Mo+W, hot-working nature will deteriorate, and cracks will occur frequently at the time of a forge. If Ti or Nb is added even if it adds Mo, W, or V, compared with 21-4N, high

temperature strength and fatigue-at-elevated-temperature intensity are improvable so that O steel, D steel and N steel, and A steel can be understood by comparing, respectively, but. It turns out that it is [ the improvement effect ] larger not to add Ti or Nb.

[0016]

[Table 1]

本発明鋼および比較鋼の化学成分（単位：mass%）

	C	Si	Mn	P	S	Ni	Cr	Mo	W	Ti	Nb	V	Al	N	Fe
本 発 明 鋼	A	0.51	0.2	9.6	0.02	0.005	4.3	21.0	—	—	—	0.35	0.02	0.35	Bal.
	B	0.42	0.3	9.1	0.03	0.003	4.5	21.5	—	—	—	0.87	0.02	0.43	Bal.
	C	0.53	0.1	10.0	0.02	0.007	4.7	20.0	4.0	—	—	0.18	0.03	0.37	Bal.
	D	0.55	0.5	9.7	0.04	0.005	3.5	20.5	1.0	2.5	—	0.30	0.02	0.40	Bal.
	E	0.52	0.3	9.5	0.03	0.004	5.0	22.0	—	4.6	—	0.20	0.04	0.33	Bal.
	F	0.37	0.7	8.7	0.04	0.006	4.0	21.3	4.8	—	—	—	0.02	0.50	Bal.
	G	0.46	0.6	9.0	0.03	0.005	4.5	20.0	2.5	1.8	—	—	0.02	0.41	Bal.
	H	0.50	0.8	9.5	0.03	0.007	4.9	22.5	—	4.6	—	—	0.02	0.32	Bal.
比 較 鋼	J	0.42	0.2	9.8	0.02	0.005	3.5	21.0	—	—	—	1.30	0.02	0.37	Bal.
	K	0.52	0.2	10.2	0.02	0.006	3.7	21.5	5.6	1.8	—	0.30	0.03	0.40	Bal.
	L	0.55	0.4	9.5	0.03	0.005	3.9	21.7	1.7	6.0	—	—	0.02	0.39	Bal.
	M	0.46	0.3	9.6	0.03	0.004	4.1	21.5	1.2	2.9	—	0.80	0.02	0.41	Bal.
	N	0.52	0.2	9.7	0.03	0.006	4.0	21.4	—	0.3	—	0.43	0.02	0.43	Bal.
	O	0.45	0.3	9.9	0.03	0.004	4.3	21.9	1.0	3.0	—	1.0	0.30	0.39	Bal.
	21-4N	0.51	0.1	9.8	0.03	0.002	3.4	21.9	—	—	—	—	0.01	0.39	Bal.
NCF751	0.05	0.3	0.2	0.01	0.002	Bal.	15.3	—	—	2.4	1.0	—	1.16	—	6.99

[0017]

[Table 2]

供試鋼の熱間加工性と材質特性

		熱間加工性*	常温引張り 破断伸び;%	900℃引張り 強度;kgf/mm <sup>2</sup>	900℃回 転 曲 げ 疲労強度;kgf/mm <sup>2</sup>
本 発 明 鋼	A	○	18	24	17
	B	○	15	27	18
	C	○	15	26	18
	D	○	16	27	18
	E	○	16	26	18
	F	○	17	25	17
	G	○	19	25	17
	H	○	18	25	17
比 較 鋼	J	△	9	27	18
	K	×			
	L	×			
	M	×			
	N	○	18	21	15
	O	○	17	22	15
21-4N		○	15	19	14
NCF751		△		28	15

\* ; ○ : 鍛造時割れなし

△ : 鍛造時一部表面微小割れあり、試験片採取可能

× : 鍛造時割れ多発、試験片採取不能

[0018]

[Effect of the Invention]Steel according to this invention has the high temperature strength and fatigue-at-elevated-temperature intensity of exhaust gas which can respond to a temperature rise. That is, the elevated-temperature tensile strength of this invention at 900 \*\* is higher than 23 kgf(s)/mm<sup>2</sup>, and its rotary bending fatigue strength at 900 \*\* is higher than 16 kgf(s)/mm<sup>2</sup>, and it can provide the heat resisting steel for exhaust valves which can secure economical efficiency and hot-working nature.